Research Article

Effect of Methyltrimethoxy Silane Modification on Yellowing of Epoxy Coating on UV (B) Exposure

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The exterior durability of epoxies is severely affected due to its poor weathering resistance. Epoxies exhibit chalking and discoloration under UV exposure caused as a result of photodegradation. The present work aims at studying the extent to which the color change and yellowing caused due to weathering under accelerated weathering conditions, of DGEBA epoxy, could be lowered by in situ modification of the epoxy polymer backbone with a silane, namely, MTMS. The epoxy resin and silane-modified epoxy resin were formulated into a TiO_2 -based white coating, applied on mild steel panels, and exposed in a UV (B) weatherometer. The color change (dE) and yellowness index (YI) values of weathered panels were evaluated using a spectrophotometer. The weathered samples were also characterized using FTIR-imaging technique to study the effect of weathering on the structural backbone of the formulated coatings. The silane-modified epoxy coatings showed lowered yellowing by 45% on UV exposure and the enhanced resistance to yellowing of the modified coatings was indicated by lowered dE and YI values. The enhanced resistance to yellowing by the silane-modified epoxy was attributed to the strengthening of the epoxy backbone by introduction of Si-O-C linkage onto the epoxy polymeric chain.

1. Introduction

Epoxies as binders are extensively used for corrosion protection in coating industry because of their excellent corrosion resistance and adhesion to substrates. However, their outdoor usage is restricted due to their poor weathering resistance. On exterior exposure, conventional epoxy coatings exhibit chalking and discoloration and lose most of their gloss in three to six months. It is generally due to the presence of aromatic moiety in epoxy polymeric backbone; they absorb at about 300 nm wavelength of light, comprising of UV light and degrade resulting in discoloration and chalking [1, 2].

Malshe and Waghoo partially modified the diglycidyl ethers of bisphenol A (DGEBA) and bisphenol F (DGEBAF) with various linear and aromatic dibasic acids [2]. The paints prepared using these resins and cured with amine terminated dimer fatty acid-based polyamide (FPA) were evaluated for their weathering characteristics by subjecting them to

accelerated and environmental weathering. It was observed that the chalk resistance and the gloss increased with the increase in the carbon length of the linear acids. Weatherable, corrosion resistant epoxy siloxane hybrid binders can be formulated with silicone intermediates, oxysilanes, and aminosilanes using the organic-inorganic chemistry. The introduction of silicone intermediates into the resin creates new resinous materials with enhanced functionality that includes heat resistance, weatherability, flame resistance, improved impact resistance, lubricity, and flexibility [3]. Resin modification methods can be divided into two categories, namely, chemical bonding method and integral blend method. In the chemical bonding method, the organic groups in the resin are reacted directly with the organic groups in the silicone intermediates; while in the integral blend method the silicone intermediate is simply mixed into the resin. The chemical bonding method generally involves a reaction with a hydroxyl group containing resin in the presence

of a catalyst. The reaction catalysts used are typically alkyl titanates, organic acids, or amine compounds. Hydroxyl and other active groups in the organic resin react with alkoxysilyl groups to produce copolymers which are useful as a resin component for manufacturing paints which have good weatherability, heat resistance, and chemical resistance [3].

There are several examples of the use of silanes to enhance the weathering behavior of wood as a result of water repellence, which prevents leaching of chemicals and wood constituents [4]. Epoxy resins were chemically modified with various silane monomers to enhance the corrosion resistance of epoxy coatings on 2024-T3 aluminum substrates and immersion studies conducted in 3.5 wt.% NaCl solution showed that the coating capacitance (Cc) decreased significantly after the silane modification, as measured by electrochemical impedance spectroscopy (EIS), indicating the higher resistance to water permeation [5]. In situ modification of epoxy polymer with silane for weathering resistance, presently, has not yet been reported and this leads to the thought of modifying the epoxy resin with silane to study the weathering behavior of the silane-modified epoxy coating.

In the present work, diglycidyl bisphenol A based epoxy resin was chemically modified with methyltrimethoxy silane (MTMS) and then formulated into a white coating, based on TiO_2 pigment. A white coating with epoxy as the binder would turn yellow in no time under UV exposure. Yellowing of epoxy is an indication of degradation, caused by chain scission reactions occurring in the epoxy polymeric backbone when exposed to UV light. The present study was an attempt to study the extent of lowering in yellowing or discoloration, achievable by the introduction of Si-O-C linkage by the silane onto the epoxy polymeric backbone. The silane-modified coating was applied on mild steel panels and subjected to accelerated UV (B) weathering and the color change and yellowness index values, evaluated during the study, showed that there was a considerable lowering of yellowing and discoloration owing to the silane modification of epoxy.

2. Experimental

2.1. Materials. Epoxy resin, diglycidyl ether of the bisphenol A (DGEBA) with EEW of 185, was obtained from DOW Chemicals (DER 331). The hardener used was an amine-based hardener, namely, diethylenetriamine (DETA) from Sigma-Aldrich (Product number D93856, CAS number 111-40-0). Xylene as solvent and dibutyltin laurate (DBTL) as catalyst were used in the silane modification of epoxy resin. Xylene was procured from MERCK chemicals (Product number 1086611000, CAS number 1330-20-7) and dibutyltin laurate (DBTL) was procured from Sigma-Aldrich (Product number 291234, CAS number 77-58-7). Methyltrimethoxy silane (MTMS) used to chemically modify epoxy was procured from Sigma-Aldrich (Product number 253006, CAS number 1185-55-3). BYK additives, namely, BYK A530 (De-foamer), BYK 333 (Wetting agent), BYK 9076 (Dispersant), and BYK 320 (Levelling agent), were used for formulation of the TiO_2 -based epoxy coating.

TABLE 1: Concentration of additives in coating formulation.

BYK A330	2% of total formulation
BYK 333	1% of total formulation
BYK 9076	1.5% of total formulation
BYK 320	0.5% of total formulation

2.2. Synthesis of Silane-Modified Epoxy Resin. A mixture of epoxy, silane in the ratio of 3:1, was charged into a three-necked flask equipped with mechanical stirrer and a reflux condenser. Xylene as solvent medium and dibutyltin laurate were added in appropriate amounts and the mixture was heated at 90–100°C for three hours with constant stirring.

The solvent and alcohol formed as byproduct were removed by heating to obtain the silane-modified resin. The epoxy equivalent weight (EEW) for the silane-modified resin was determined by titration method to calculate the desired phr value of the hardener.

FTIR spectroscopy was used to characterize the structure of unmodified epoxy resin and the silane-modified epoxy resin. The viscous resin samples were directly applied by dabbing onto KBr pellets. The IR spectra were recorded on a Perkin Elmer ATR spectrum 100 FTIR spectrometer in the range of 400–4000 cm^{-1} at a resolution of 4 cm^{-1} for 32 scans.

2.3. Preparation of Coated Samples. A TiO_2 -based white coating was formulated with 35% pigment concentration and 50% resin concentration and the rest with the appropriate concentrations of additives and solvent. The additive concentration in the coating is tabulated in Table 1.

The mild steel samples to be coated were degreased, cleaned, and then roughened mechanically with abrasive paper (emery paper grade number 100). The formulated TiO_2 -based white coating was applied using brush on the surface treated MS substrate panels so as to achieve uniformly coated panels with good finish and then was allowed to hard cure. The coated panels were allowed to dry at room temperature for a day, followed by oven cure for 5 hours at 80°C.

2.4. Weathering Test. The unmodified and silane-modified epoxy coated MS panels were subjected to accelerated weathering in a UV (B) weatherometer (QUV weatherometer, Q-Lab Products & Services) equipped with UV (B) 313 nm lamps. The test cycle in UV (B) weatherometer is comprised of 4 h of UV (B) simulation at 60°C followed by 4 h of condensation (UV (B) lights off during condensation) at 50°C as per accordance of ASTM G-154.

Both unmodified and silane-modified epoxy coated panels, exposed in UV (B) weatherometer, were characterized for color change (dE) and yellowness index (YI) using a spectrometer (BYK-Gardener Spectrometer) equipped with Color-Lab Quality Control software based on CIE Color Space Model. The coatings exposed in UV (B) weatherometer were characterized for color change (dE) and yellowness index (YI) using a spectrometer (BYK-Gardener Spectrometer) equipped with Color-Lab Quality Control software.

The instrument settings were done with the “color space” as “CIE Lab,” the measurement mode with observer angle 10°, and the illuminant D65 (D65 illuminant was used which is similar to day light spectra). Color of the coating was represented by using “*L*,” “*a*,” and “*b*,” where “*L*” is the lightness, “*b*” is the representation of blue or yellowness, and “*a*” is the representation of green or redness. The color spectrophotometer measured overall color difference between two different samples, which is represented as *dE*. The data were reported on *L*, *a*, and *b* scales and overall color difference was given in the following equation [1]:

$$dE = [\Delta L^2 + \Delta a^2 + \Delta b^2]^{1/2}, \quad (1)$$

where $\Delta L = L_2 - L_1$, $\Delta a = a_2 - a_1$, and $\Delta b = b_2 - b_1$.

Respective numbers 1 and 2 are denoted to samples before and after the exposure test.

Yellowness index is a number calculated from spectrophotometric data that describes the change in color of a test sample from clear or white toward yellow. This test is most commonly used to evaluate color changes in a material caused by real or simulated outdoor exposure [1]. The yellowness index is measured as per ASTM D 1925 and is formulated as follows:

$$YI = \frac{100 (1.28X_{CIE} - 1.06Z_{CIE})}{Y_{CIE}}. \quad (2)$$

As per ASTM D 1925, the conditions for measurement are as follows: illuminant: C and standard observer function: 2°, denoted by C/2°. *X*, *Y*, and *Z* are the tristimulus values and 1.28 and 1.06 are the coefficients as per C/2° conditions.

FTIR studies of the unexposed and UV (B) exposed coated panels were carried out to understand the weathering behavior of the epoxy coating FTIR Imaging instrument (Model: 3000 Hyperion Microscope with Vertex 80 FTIR System, Bruker).

3. Results and Discussion

3.1. FTIR Analysis of Silane-Modified Epoxy Resin. The FTIR spectrum of unmodified epoxy resin is as shown in Figure 1. For pure epoxy resin, the band at 3500 cm⁻¹ is assigned to (–OH) stretching. The bands at 2970 and 1390 cm⁻¹ are characteristics of (–CH₃) asymmetric and symmetric stretching, and the bands at 2877 and 1461 cm⁻¹ are assigned to asymmetric and symmetric stretching mode of (–CH₂). The band at 910 cm⁻¹ is the characteristic absorption of epoxide groups. The band at 1246 cm⁻¹ is assigned to the ether bonds in epoxide groups. The absorption peaks at 1604, 1520, and 828 cm⁻¹ are the characteristics of substituted aromatic rings in epoxy resin.

Figure 2 shows the comparative FTIR spectra of unmodified and silane-modified epoxy resin. The spectrum of silane-modified epoxy resin was observed to be similar to that of unmodified epoxy resin, except for the intensification of peaks at 1000–1100 cm⁻¹ which is due to the formation of Si–O–C bonds in the silane-modified epoxy resin [5, 6]. The probable schematic of the reaction between epoxy resin and MTMS is shown in Figure 3.

FIGURE 1: FTIR spectra of neat DGEBA-based epoxy resin.

FIGURE 2: FTIR spectra of neat epoxy resin and silane-modified epoxy resin at 1000–1100 cm⁻¹ wavenumber region.

3.2. Color Change (*dE*) and Yellowness Index (*YI*) Measurements. The unmodified and silane-modified epoxy resin formulated TiO₂-based white coatings with a thickness in the range of 80–100 microns were exposed for five cycles in UV (B) weatherometer. The color change (*dE*) and change in yellowness index (*YI*) values for the UV (B) exposed unmodified epoxy and silane-modified epoxy coating systems at different testing intervals are as shown in Figures 4 and 5.

The spectrophotometric results for UV (B) weathered epoxy samples showed that the silane modification helped in lowering the *dE* and *YI* values indicating that the silane modification imparted resistance to yellowing of the epoxy system under study. The extent of yellowing resistance, offered by the MTMS-modified epoxy coating systems, was determined by evaluating the percentage reductions in color change (*dE*) and yellowness index (*YI*) during the exposure. The percentage reduction values were calculated as follows.

Suppose that after 2 UV (B) cycles in weatherometer

$$\text{Neat Epoxy} = A, \quad (3)$$

$$\text{Modified Epoxy} = B, \quad (4)$$

FIGURE 3: Schematic of synthesis of MTMS-modified epoxy resin.

FIGURE 4: dE plot for neat and MTMS-modified epoxy coatings after UV (B) exposure.

where A and B are dE (or YI value) after the weathering cycle; then,

$$\% \text{Reduction in dE (or YI)} = \left[\frac{A - B}{A} \right] \times 100. \quad (5)$$

The percentage reduction values in color change and yellowness index thus calculated are tabulated in Tables 2 and 3, respectively.

The better yellowing resistance of the silane-modified epoxy coating on weathering under UV (B) exposure,

FIGURE 5: YI plot for neat and MTMS-modified epoxy coatings after UV (B) exposure.

compared to that of neat epoxy coating, is attributed to the formation of Si-O-C bond in the backbone of epoxy resin. The bond dissociation energy of C-O bond as in case of unmodified epoxy is 358 kJ/mole, while the bond dissociation energy for the grafted Si-O bond as in the silane-modified epoxy is 452 kJ/mole. Thus, there is an overall bond strengthening for the silane-modified epoxy on MTMS modification which imparts better weathering resistance compared to unmodified epoxy on UV (B) exposure. MTMS modification of the epoxy lowered color change and yellowing by 45% on UV (B) exposure. The lowering effect was observed even after 80 hours of UV (B) exposure indicating that the silane

FIGURE 6: Structure of DGEBA-based epoxy resin.

TABLE 2: The percentage reduction in dE at different UV (B) testing intervals.

System	The percentage reduction in dE at different UV (B) testing intervals				
	16 hours	32 hours	48 hours	64 hours	80 hours
MTMS : DGEBA = 1 : 3	45%	45%	45%	45%	44%

TABLE 3: The percentage reduction in dYI at different UV (B) testing intervals.

System	The percentage reduction in dYI at different UV (B) testing intervals				
	16 hours	32 hours	48 hours	64 hours	80 hours
MTMS : DGEBA = 1 : 3	46%	46%	46%	46%	45%

modification imparted stabilized weathering resistance to the epoxy coatings.

3.3. FTIR Analysis of UV (B) Weathered Coated Panels. The vulnerable sites on the epoxy polymeric backbone are the aromatic ether group due to its reactivity and the isopropylidene group owing to the cleavage of $\text{CH}_3\text{-C}$ bond, as shown in Figure 6 [7].

The notable change in the unweathered and UV (B) weathered coated panels for both unmodified and silane-modified epoxy systems was intensification at carbonyl region ($1600\text{--}1700\text{ cm}^{-1}$) along with appearance of quinone methide peak at $1650\text{--}1657\text{ cm}^{-1}$ due to photooxidation of isopropylidene group [8–10]. The comparative FTIR spectra for the unmodified and silane-modified epoxy coated panels after first two cycles (16 hours) and 5 cycles (80 hours) of UV (B) exposure causing noticeable yellowing are as shown in Figures 7, 8, and 9.

The better performance of MTMS-modified epoxy under UV (B) exposure than that of unmodified epoxy system can be explained from the FTIR results as shown in Figure 9. The MTMS-modified epoxy coating showed lower intensity peak at 1654 cm^{-1} attributed to formation of quinone methide structure considered responsible for discoloration of epoxies on weathering in comparison to the unmodified epoxy coating [9]. The FTIR results were further affirmed by evaluating the carbonyl index for the weathered epoxy coatings. Carbonyl index method detects the creation of carbonyl groups within the weathered material indicating degradation through oxidation after accelerated weathering. The carbonyl index values for the most intense peak observed for all

FIGURE 7: Comparative FTIR spectra of neat epoxy coating before and after UV (B) exposure.

weathered coatings observed at 1654 cm^{-1} with reference to the peak at 2877 cm^{-1} for methylene ($-\text{CH}_2-$) group which underwent minimal change on weathering were calculated as per the standard formula [11–13]:

$$\text{Carbonyl Index } (1654\text{ cm}^{-1}) = \frac{I_{\text{absorbance at } 1654\text{ cm}^{-1}}}{I_{\text{absorbance at } 2877\text{ cm}^{-1}}} \quad (6)$$

The carbonyl index value is an indicative of the susceptibility of photooxidation for polymers on weathering. As epoxies are prone to chain scission and undergo photooxidation on weathering forming carbonyl compounds, carbonyl

FIGURE 8: Comparative FTIR spectra of MTMS-modified epoxy coating before and after UV (B) exposure.

FIGURE 9: Comparative FTIR spectra of neat and MTMS-modified epoxy coatings after 2 and 5 cycles of UV (B) exposure.

index value is a quantitative measure of photodegradation. The carbonyl index values thus obtained were plotted as shown in Figure 10.

As observed in Figure 10, MTMS-modified epoxy coating showed lower carbonyl index value compared to neat epoxy coating, indicating lower chain scission and consequently less yellowing. The spectrophotometric results were, thus, evidenced by FTIR results and carbonyl index measurements. It was, thus, confirmed that the Si–O–C linkage grafted onto the epoxy polymeric backbone offered resistance to the chain scission reaction on UV (B) exposure and caused lowered yellowing and discoloration.

FIGURE 10: Carbonyl index plot for neat epoxy and MTMS-modified epoxy coatings after 2 and 5 cycles of UV (B) exposure.

4. Conclusions

The silane modification was found to effectively enhance the yellowing resistance of the epoxy coating during UV (B) exposure. MTMS modification of epoxy resin lowered color change and yellowing by 45% for the formulated coatings and this lowering was effective even at extended UV (B) exposures. The Si–O–C linkage grafted onto the epoxy polymeric backbone effectively offers resistance to chain scission reactions and consequently to photodegradation, imparting weathering resistance to the epoxy polymeric backbone. The FTIR results and carbonyl index measurements confirmed the spectrophotometric results. The carbonyl index values were effectively lowered for the weathered MTMS-modified epoxy coating compared to the neat epoxy coating.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

References

- [1] G. Wypych, *Handbook of Material Weathering*, ChemTec, 2003.
- [2] V. C. Malshe and G. Waghoo, "Chalk resistant epoxy resins," *Progress in Organic Coatings*, vol. 51, no. 3, pp. 172–180, 2004.
- [3] "Silicones for resin modification," 2011, http://www.silicone.jp/e/catalog/pdf/ResinModification_e.pdf.
- [4] S. Donath, H. Militz, and C. Mai, "Weathering of silane treated wood," *European Journal of Wood and Wood Products*, vol. 65, no. 1, pp. 35–42, 2007.
- [5] W. G. Ji, J. M. Hu, L. Liu, J. Q. Zhang, and C. N. Cao, "Improving the corrosion performance of epoxy coatings by chemical modification with silane monomers," *Surface and Coatings Technology*, vol. 201, no. 8, pp. 4789–4795, 2007.

- [6] O. H. Teresa and C. K. Choi, "Comparison between SiOC thin films fabricated by using plasma enhance chemical vapor deposition and SiO₂ thin films by using fourier transform infrared spectroscopy," *Journal of the Korean Physical Society*, vol. 56, no. 4, pp. 1150–1155, 2010.
- [7] B. Mailhot, S. Morlat-Therias, M. Ouahioune, and J. L. Gardette, "Study of the degradation of an epoxy/amine resin, 1," *Macromolecular Chemistry and Physics*, vol. 206, no. 5, pp. 575–584, 2005.
- [8] P. G. Kelleher and B. D. Gesner, "Photo-oxidation of phenoxy resin," *Journal of Applied Polymer Science*, vol. 13, no. 1, pp. 9–15, 1969.
- [9] G. Zhang, W. G. Pitt, S. R. Goates, and N. L. Owen, "Studies on oxidative photodegradation of epoxy resins by IR-ATR spectroscopy," *Journal of Applied Polymer Science*, vol. 54, no. 4, pp. 419–427, 1994.
- [10] J. L. Down, "The yellowing of epoxy resin adhesives: report on high-intensity light aging," *Studies in Conservation*, vol. 31, no. 4, pp. 159–170, 1986.
- [11] J. V. Gulmine and L. Akcelrud, "FTIR characterization of aged XLPE," *Polymer Testing*, vol. 25, no. 7, pp. 932–942, 2006.
- [12] T. Corrales, F. Catalina, C. Peinado, N. S. Allen, and E. Fontan, "Photo oxidative and thermal degradation of polyethylenes: interrelationship by chemiluminescence, thermal gravimetric analysis and FTIR data," *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 147, no. 3, pp. 213–224, 2002.
- [13] A. L. Andrady, J. E. Pegram, and Y. Tropsha, "Changes in carbonyl index and average molecular weight on embrittlement of enhanced-photodegradable polyethylenes," *Journal of Environmental Polymer Degradation*, vol. 1, no. 3, pp. 171–179, 1993.